



Improvements in or relating to cracking of hydrocarbons

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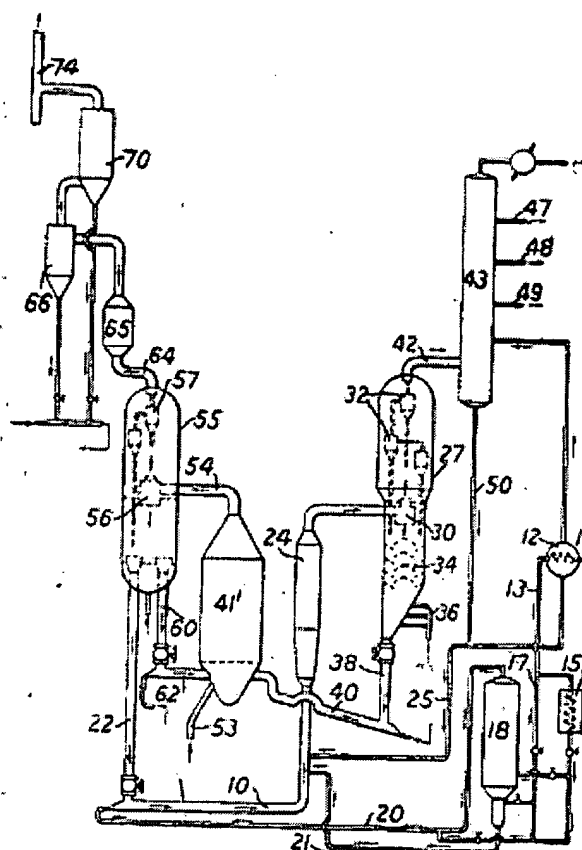
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Abstract of GB767312

Hydrocarbon oils are cracked by forming a suspension of particles of cracking catalyst having a specific gravity of 1.6 to 2.7 in the vaporized oil, passing the suspension at a temperature between 800 DEG <PICT:0767312/III/1> and 1100 DEG F. and at a vapour velocity of 8 to 50 feet per second through a vertical elongated reaction zone having a length to diameter ratio in the range from 4:1 to 20:1, maintaining the ratio weight of feed passing through the reaction zone in an hour/weight of catalyst in the reaction zone at any particular instant in the range from about 20:1 to about 300:1, and separating the cracked product vapours from the suspension discharged from the reaction zone. The method may be used for cracking gas oil, heavy naphtha, and kerosene. Silica-alumina, silica-magnesia, and silica-zirconia catalysts may be used. Gas oil, introduced through line 11, is heated to 450 DEG F. in heat exchanger 12, and is then passed through line 13 which divides into two streams. One stream is introduced via line 17 into the lower part of vaporizer 18. The other stream is raised to 840 DEG F. in furnace 15 and is then introduced into vaporizer 18, which is maintained at a temperature of 825 DEG F. and a pressure of 40 psig. Vapours from vaporizer 18 travel through line 20 to the base of conduit 22 where hot silica-alumina catalyst (particle diameters of 20 to 80 microns) is added, and forms a suspension in the vapour stream. Liquid hydrocarbon recycle material is added through line 25 to the suspension while it is flowing through line 10, and liquid from vaporizer 18 is added via line 21. Both these liquid streams become vaporized in line 10. The suspension then enters reaction zone 24, which is maintained at a temperature of 930 DEG F. and a pressure of 30 psig. The reaction zone has an overall length of 55 feet; its internal diameter is 8 feet for the upper 35 feet of its length, which tapers for its lower 20 feet of length to 6 feet internal diameter.



The suspension passes through zone 24 at a superficial gas velocity of 11 feet per second. The catalyst to oil ratio in the suspension is about 4.6; and the weight ratio of feed passing through the reactor per hour to the weight of catalyst in the reactor is about 77. The suspension discharged from zone 24 is introduced into distributor box 30, which is disposed in the middle section of separating vessel 27. Part of the suspension flows into the upper section of vessel 27, which is provided with cyclones 32; and the remainder descends into the lower section, which is provided with baffle plates 34 and is supplied with stripping steam via manifold 36. The cracked products leave vessel 27 through conduit 42, and are introduced into the lower section of fractionation tower 43. Tower 43 is operated at a top temperature of 275 DEG F. and a bottom temperature of 700 DEG F., the pressure therein being 22 psig. Light hydrocarbons and gasoline are withdrawn from the head of the tower. Heating oil is withdrawn from the tower via line 47, light gas oil is withdrawn via line 48, and heavy gas oil is withdrawn via line 49. A heavier fraction is withdrawn from tower 43 by a line 50 which connects into line 25, and is recycled to the reaction zone 24. Stripped catalyst flows out of the base of vessel 27 through conduit 38, and is then carried by air through conduit 40 into regenerator 411. Additional air is introduced into the regenerator through line 53; and the regenerator is maintained at a temperature of 1100 DEG F. and a pressure of 11 psig, whereby the carbonaceous deposits are removed from the contaminated catalyst by combustion. The regenerated catalyst is carried via line 54 and distribution box 56 into vessel 55, which is provided with cyclones 57. The regenerated catalyst is separated from the flue gas in vessel 55; some of the regenerated catalyst is withdrawn through conduit 22 and mixed with fresh feed, while the remainder is recycled to the regenerator via conduits 60 and 62. Flue gas at about 1000 DEG F. is withdrawn from vessel 55 via conduit 64, and passes through waste heat boiler 65. The cooled flue gas is then passed through cyclone 66 where the majority of the catalyst fines are removed; the remainder of the catalyst fines are removed from the flue gas by electrical precipitators 70. The flue gas is finally discharged into the atmosphere via stack 74. The catalyst fines are returned to regenerator 411.

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PATENT SPECIFICATION



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COMPLETE SPECIFICATION

Improvements in or relating to Cracking of Hydrocarbons.

We, ESSO RESEARCH and ENGINEERING COMPANY, formerly known as STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the Laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the cracking of hydrocarbons.

In brief, this invention provides a method of cracking hydrocarbons which comprises forming a suspension of a finely divided cracking catalyst having a specific gravity in the range between about 1.6 and 2.73 in a vaporized hydrocarbon oil at a temperature in the range between 800° and 1100°F., flowing said suspension at said temperature at a vapour velocity in the range between about 8 and about 50 feet per second through a vertical elongated reaction zone having a length-to-diameter ratio in the range from about 4 to 1 to about 20 to 1, maintaining the ratio:

weight of feed passing through the reaction zone in an hour

weight of catalyst in reaction zone at any particular instant

in the range from about 20 to 1 to about 300 to 1 to crack the hydrocarbon feed to desirable products, and recovering the said products from the suspension discharged from the reaction zone.

The said ratio is preferably from 70:1 to 250:1.

A preferred temperature range for the cracking reaction is from about 900° to about 1000°F. with quite desirable results being obtained at about 930°C.

Pressures employed in the improved cracking operation may range from about atmospheric pressure to about 50 psig (pounds per square inch gauge) with preferred range of pressures from about 20 to 50 about 35 psig.

It is undesirable to flow the suspension at a superficial gas velocity less than about 8 feet per second and the preferred range is from 8 feet per second to about 20 feet per second. Desirable results may be obtained in the range from about 10 to about 15 feet per second.

Desirable results are obtained in a vertical elongated reaction zone having a length-to-diameter ratio of about 7:1. Very good results may be obtained with a weight ratio of feed per hour to catalyst in the reaction zone in the range from about 70:1 to about 250:1.

Too, desirable results may be obtained by maintaining the catalyst rate in the operation depending on the velocity in the range of 8 to 50 feet per second in a maximum amount of 1 ton per second for the minimum velocity and a maximum amount of about 12 tons per second for the maximum velocity. At a velocity of about 20 feet per second the catalyst rate would be maintained up to about 4.5 tons per second. Thus, the catalyst loading in the reaction zone may be expressed by pounds per square foot. This may be expressed as catalyst loading in the reaction zone and should not exceed 36 pounds per second per square foot for a gas velocity in feet per second of 8, and should not exceed 180 pounds per second per square foot for a gas velocity in feet per second of 20 or about 540 pounds per second per square foot at a gas velocity in feet per second of about 50. Employing these conditions, it is possible to obtain the beneficial results of the present invention.

The feed stock employed in the present

(Price 3/-.)

Price 4/- 60

invention is preferably a gas-oil hydrocarbon such as one obtained from crude petroleum. However, other gas-oil fractions may be used. For example, the heavy oil produced in the cracking operation or unconverted portions of the feed stock may form a component of the reaction feed. It is also contemplated that gas-oils produced from thermal cracking operations may suitably be charged to the process of the present invention. It is contemplated that residual crude petroleum fractions may be charged as the feed stocks to the process of the present invention. The present invention may utilize as feed hydrocarbon the cracking stocks now used in either thermal or catalytic cracking of hydrocarbons and thus may encompass a wide range of feed stocks. Under some conditions, it may be desired to crack lighter fractions such as those in the heavy naphtha and kerosene boiling range, say, from about 400° to about 750°F. Solvent extracts containing large percentages of aromatic hydrocarbons may also form the feed stock to the present invention. Crude residues remaining after removal of valuable lubricating oil and other fractions may be charged to the process of the present invention.

The invention will be further illustrated by reference to the accompanying drawing, in which the single figure is a flow diagram of a preferred mode of practicing the invention. Referring now to the drawing, numeral 11 designates a charge line through which a gas-oil fraction is introduced into the system from a source not shown. This gas-oil fraction passes through heat exchanger 12 wherein it picks up heat by heat exchange and is heated to a temperature of about 450°F. The heated gas-oil then is discharged from heat exchanger 12 by way of line 13 and may be split into two streams, one stream flowing by way of line 14 into a furnace 15 containing a coil 16 wherein the temperature of the gas-oil is raised to a temperature of about 840°F. The other stream flows by way of line 17 into the lower portion of a vaporizer drum 18. The pre-heated stream from furnace 15 flows by line 19 also into vaporizer 18 at a point in the lower section of vaporizer 18 but above the point where the stream from line 17 is introduced.

The relative amounts of streams introduced by lines 17 and 19 are in the approximate ratio of about 1:6.

In vaporizer 18, conditions may approximate a temperature of 825°F. and a pressure of about 40 psig. Under these conditions, there is removed from the top of vaporizer 18 by way of line 20 a vaporous fraction, and there is removed from the bottom of vaporizer 18 by line 21 a liquid fraction.

The vaporous fraction in line 20 is routed thereby into a conduit 10 where it is admixed with a finely divided cracking catalyst which is introduced from conduit 22, controlled by a valve 23. In conduit 10, the finely divided catalyst is formed into a suspension in the vaporous stream introduced by line 20, and the suspension then flows into the lower end of a vertical elongated reaction zone 24. At the entrance to the vertical elongated reaction zone 24, the suspension has added to it the liquid stream from line 21, and downstream from the point of addition of the liquid stream there is added to the suspension a liquid hydrocarbon feed introduced by line 25 from a later stage in the process, which will be described in more detail hereinafter.

If desired and depending on the volatility or other characteristics of the feed stock, the feed stock may be by-passed around the vaporizer 18 through line 80 controlled by valve 81. When operating in this manner, the feed may be routed through furnace 15 by line 14 and branch line 83, valve 82 being opened and valve 84 in line 17 and valves 85 and 87 being closed. Alternatively, the feed stock may be routed through line 17 and branch line 86 which connects into line 80 by opening valves 84 and closing valves 82 and 85, valve 87 remaining closed. When passing a liquid feed stock through line 20 the heat for vaporization of the feed stock is provided by the hot catalyst when the two are admixed in line 10.

The suspension then carrying the liquid stream introduced by line 10 and the liquid hydrocarbon feed introduced by line 25 flows upwardly through reaction zone 24. Of course, it is understood that the liquid hydrocarbon streams introduced by lines 21 and 25 also become vaporized under the conditions prevailing in line 10 and the reaction zones 24. Operations may be conducted in reaction zone 24 to maintain a temperature of about 930°F., a pressure of 30 psig, and the suspension in the zone may contain about 10 tons of catalyst.

After passage through the elongated reaction zone 24, the several hydrocarbon streams introduced therein have been substantially cracked to desirable products which are contained in the suspension. This suspension containing the desirable products flows by way of a conduit 26 into a catalyst vessel 27 which is provided with an upper section 28, which may be termed a spent catalyst section, and a lower section 29, which may be termed a catalyst stripper section.

The suspension containing desirable products is introduced into the vessel 27 through a distributor box 30 which is provided with a riser 31 which allows the catalyst and vaporized products to dis-

charge upwardly in section 27 and also allows the products and suspension to be discharged downwardly into section 29. The upper section 28 is provided with cyclones 32, which are well known to the art. These cyclones 32 are interconnected to allow the gases and desirable products to flow from the lower of the cyclones sequentially through the cyclones to ensure maximum separation of the products from the catalyst. The cyclones are provided with dip legs 33 which discharge the catalyst downwardly into the vessel 27 and specifically into the sections 28 and 29. The catalyst separated from the desirable products flows downwardly in stripper 29, which is provided with baffle plates 34 which ensure contact of the catalyst with stripping steam or a stripping gas which is introduced into the section 29 by line 35 through manifold 36. The steam flowing countercurrently to the descending catalyst removes volatilizable carbonaceous material from the catalyst which flows downwardly in the catalyst stripper section 29 and outwardly therefrom through the cone-shaped section 37 into a conduit 38 controlled by a valve 39. The conduit 38 connects into a transverse conduit 40 which is provided with line 41, through which air is introduced into conduit 40. The air picks up the stripped catalyst and discharges it by way of conduit 40 into a regenerator vessel 41' where a regeneration operation takes place which will be described in more detail hereinafter.

The products from the cracking reaction substantially separated from catalyst withdrawn from vessel 27 by way of conduit 42, which introduces the desirable products into the lower section of a fractionation zone 43, where the desirable products are separated and recovered. The fractionation zone may comprise a plurality of distillation towers which may be shown for convenience as a single distillation tower.

Fractionation zone 43 may operate at a top temperature of about 275°F. and a bottom temperature of about 700°F. A pressure of about 22 psig may be maintained on the fractionation zone 43.

Under these conditions, there is removed from zone 43 by line 44 a fraction containing gaseous materials and the lighter fractions including the desirable vaporous hydrocarbons having three or more carbon atoms in the molecule. For example, the stream withdrawn by line 44 may contain propane, propylene, butanes, and butylenes and the higher boiling hydrocarbons. This stream also contains the desirable cracked gasoline which may be suitably recovered. The stream in line 44 is passed through a condenser and cooler 45 and then discharged by line 46 to stabilization and recovery facilities not shown. A heating oil

fraction may be withdrawn from fractionation zone 43 by line 47, and light and heavy cycle gas-oil fractions may be withdrawn from zone 43 by lines 48 and 49, respectively. A heavier fraction is withdrawn from zone 43 by line 50 which connects into line 25 and forms a source for the feed hydrocarbon introduced by line 25 into zone 24. Part of the heavier fraction is re-cycled to the fractionator by way of lines 51 and 52 and heat exchanger 12. During the cracking operation in zone 24 there is laid down on the catalyst volatilizable carbonaceous material and coke. This material, if allowed to remain on the catalyst, would impair the cracking operation; however, it is desirable to have a small amount of coke or carbonaceous material on the catalyst since this allows the heat necessary for the process to be obtained at least in part by burning this material from the catalyst. It is necessary to remove this material from the catalyst to regenerate it to allow re-use of the catalyst in the cracking operation. To this end, the air introduced into line 40 by line 41 is supplemented by air introduced into reaction zone 41' by line 53 connecting to a compressor or some other source of air. By controlling the oxygen content of the air or other free oxygen containing gas introduced into regeneration zone 41', it is possible to conduct a combustion or burning operation in regeneration zone 41' such that catalyst is substantially freed of unstrippable carbonaceous material and coke and then may be re-used in the process. For example, the regenerator 41' may contain about 100 tons of catalyst which is contacted with about 47,000 standard cubic feet of air per minute causing combustion of the combustible material on the catalyst. The other conditions for maintenance for the combustion operation may be a temperature of about 1100°F. and a pressure of 11 psig.

The regenerated catalyst in a suspension of the combustion products then flows from regeneration zone 41' by way of line 54 into a regenerated catalyst vessel 55 through a distribution box 56.

The regenerated catalyst vessel 55 is provided with separation means illustrated by cyclones 57 which may be arranged for sequential flow of the suspension therethrough to obtain maximum separation of catalyst from the combustion products, which may be termed flue gas. The cyclones 57 are provided with dip legs 58 which discharge the separated catalyst back into the vessel 55. This vessel may contain catalyst at a temperature of about 1125°F. and is of a suitable size to provide storage for about 50 tons of regenerated catalyst. Air may be introduced into the vessel 55 by line 59.

Conduit 22 withdraws the catalyst from the vessel 55 for mixing with the feed, as has been described, while conduit 60 controlled by valve 61 provides re-cycle of catalyst from vessel 55 into regenerator 41'. Conduit 60 connects into a conduit 62 into which is introduced by line 63 a sufficient amount of air to carry the catalyst from conduit 60 through conduit 62 into vessel 10 41'. The amount of air introduced by line 63 supplements the air introduced by lines 41 and 53.

The combustion products of flue gas from which catalyst has been separated by cyclones 57 in vessel 55 is withdrawn from vessel 55 by conduit 64, which is provided with a waste heat boiler 65 which may be a bank of tubes surrounding or arranged in the conduit 64. The waste heat boiler 65 20 recovers some of the heat contained in the flue gas which may be at a temperature of 1,000°F. The flue gas then flows into cyclone 66 which serves to remove catalyst fines not removed by cyclones 57 from the 25 combustion products. These catalyst fines may have particle diameters in the range from about 0 to 20 microns. The separated catalyst fines are discharged from cyclones 66 by way of line 67 into a line 68, 30 and the disposition for these fines will be described further hereinafter.

The flue gas substantially free of catalyst fines but containing a small amount thereof is then routed by conduit 69 into electrical 35 precipitators 70, which may be of a conventional type where the residual amount of fines is substantially removed from the flue gas. These fines are discharged by line 71 into line 68. Air may be introduced into 40 line 68 by line 72 in an amount sufficient to transport the fines to regenerator 41'.

A flue gas substantially free of fines is then discharged into the atmosphere by way of a conduit 73 which connects into a 45 stack 74. It is not practical to separate completely all of the fines from the flue gas and a minimum amount of catalyst fines may be discharged through stack 74. In fact, it may be desirable to discharge a 50 minimum amount of catalyst fines, since discharge of a small amount and replacement thereof with fresh catalyst serves to maintain the activity of the catalyst at a high level.

55 By virtue of an operation as described in connection with the drawing, it is possible to achieve substantially improved and unexpected results in cracking hydrocarbons. Thus, with the present invention, it 60 is possible to conduct a cracking operation at high efficiencies with the laying down of less coke on the catalyst than is possible in conventional operations. It is possible to produce substantially increased amounts 65 of gasoline hydrocarbons without decreas-

ing the amount of desirable butanes and butylenes.

Also in the practice of the present invention, it is possible to charge a substantially greater amount of feed stock to the 70 system than was possible in conventional operations. Thus, in the improved process it is possible to increase the throughput by 50%, while maintaining the same degree of conversion or, alternatively, the degree of 75 conversion may be increased with the same charge rate. This is accomplished at a lower temperature with less catalyst and with less formation of coke than was obtained in conventional operations. 80

While the reaction zone 24, as shown in the drawing, provides for upward flow of the suspension of catalyst in hydrocarbon, the beneficial results of practicing the present invention may also be obtained when 85 the catalyst and reactants flow downwardly in the reactor. To accomplish downward flow, suitable spacial re-arrangement of the apparatus elements in the catalyst cycle may be required. 90

In a specific commercial operation, a gas-oil fraction is divided into a vapor feed and a liquid feed and the vapor feed admixed with catalyst to form a suspension. The liquid feed is then mixed with the 95 suspension, and the admixture has added to it a re-cycle feed such as one obtained from line 50 in the drawing. This suspension the flows to a vertical elongated reaction zone having a total length of about 100 55 feet and having an internal diameter for 35 feet of its length of about 8 feet, which tapers for its lower 20 feet of length down to about 6 feet internal diameter. The suspension is flowed through the reaction zone 105 at a superficial gas velocity of about 11 feet per second and a catalyst-to-oil ratio of about 4:6. The ratio weight of feed passing through reaction zone in an hour —weight of catalyst in reaction zone at 110 any particular instant—is about 77. Operating at 54% conversion on the feed at 930°F. gave substantially improved results. Thus, a carbon reduction of 24% was obtained at 10% re-cycle of fraction such as 11: in line 50, while charging about 51,000 barrels per day of fresh feed. These results are substantial improvements and allow the production of substantially increased 120 amounts of valuable products over that possible heretofore.

The catalyst employed in the practice of the present invention may be a silica-alumina catalyst having particle diameters in the range of about 0 to about 100 microns with 120 a major amount of the catalyst having particle diameters in the range from about 20 to about 80 microns.

While it is preferred to use silica-alumina catalyst, the invention may be prac- 13

bonaceous material and coke from it in the suspension of finely divided catalyst in the said gas, and separating combustion reaction products from the thus regenerated catalyst.

7. A method according to any one of the preceding claims, in which a stream of 60 liquid hydrocarbons is separated from the said desirable products and at least a portion of this stream is re-cycled and admixed with the suspension of finely divided catalyst in vaporized hydrocarbon feed. 65

8. A method according to any one of the preceding claims, in which the suspension of finely divided catalyst in vaporized hydrocarbon feed has been made by introducing a liquid hydrocarbon feed into a stream of the hot catalyst which vaporizes the liquid hydrocarbon.

9. A method according to any one of Claims 1-7, for cracking a gas-oil, in which the suspension, of finely divided catalyst 70 in vaporized hydrocarbon feed has been made by heating the gas-oil to from 400 to 900°F., separating the gas-oil into a major quantity of a vaporous fraction and a minor quantity of liquid fraction, and admixing 75 the catalyst in the vaporous fraction; and in which the liquid fraction is admixed with the suspension.

10. A method according to Claim 9 as dependent on Claim 7, in which the liquid 80 fraction from the gas-oil is admixed with the suspension upstream from the re-cycled stream.

11. A method according to any one of the preceding claims, in which the reaction zone has a length-to-diameter ratio of 7:1

12. A method according to any one of the preceding claims, in which the superficial vapor velocity of the suspension is from 10 to 15 feet per second.

13. A method according to any one of the preceding claims, in which the specific gravity of the catalyst particles is from 1.92 to 2.40.

14. A method for the catalytic cracking of petroleum hydrocarbons substantially as hereinbefore described

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- 45 6. A method according to Claim 4, including the additional steps of admixing the separated catalyst containing carbonaceous material and coke with a gas containing free oxygen in an amount sufficient to support a combustion operation and to form
50 a suspension of the said catalyst containing coke and carbonaceous material, regenerating the catalyst by burning car-

767,312 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

